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DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 65

DETERMINATION OF OIL AND RESIN IN VARNISH

BY

E. W. BOUGHTON, Associate Chemist

Bureau of Standards

ISSUED FEBRUARY 19, 1916



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DETERMINATION OF OIL AND RESIN IN VARNISH

E. W. Boughton

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I. INTRODUCTION

In spite of the fact that several methods have been published for the determination of oil and resin in varnish, there is a noticeable lack of information regarding the accuracy of the results obtained by such methods, due largely to failure to test the procedures with varnishes of known composition and history. It seemed desirable, therefore, to obtain such information and to devise, if possible, a method which would be satisfactory. While the proposed method has not yielded results which are as accurate or as concordant as might be desired, it is believed that it is sufficiently accurate to be of practical value in varnish analysis. It is shown that several methods to be found in the literature are not reliable for all types of oil varnish.

II. THE MANUFACTURE AND COMPOSITION OF OIL VARNISH

In the manufacture of oil varnish ¹ the resins (commonly called "gums" in the trade) are heated until melted, and at the proper time the oil and driers (or oil containing driers) are added. The mass is mixed and heated until, in the judgment of the varnish maker, it is ready to be cooled and thinned. The varnish is filtered and run into settling tanks, where it is aged. The time of heating, temperature, etc., depend upon the nature of the varnish and vary greatly for different kinds.

Many different *resins* are used, among which are kauri, Zanzibar, Pontianak, manila, and rosin (colophony). As a rule, the harder resins are more valuable. The various grades and types of each resin are designated according to size as "bold," "nubs," "seeds," and "dust." The principal *oils* used are linseed oil (refined and treated by various processes) and Chinese wood oil (tung oil). The common *thinners* are turpentine and light mineral oils. Compounds of lead and manganese are used as *driers*, and if rosin is present lime is generally added to harden it. The product obtained by heating a resin at high temperatures, called by Sabin ² "pyro-copal," is very different in nature from the original resin, and when combined with the oil, imparts to a varnish properties which have so far been obtained only in this way. Further information regarding the manufacture of varnish may be found in many text books.³

III. METHODS OF VARNISH EXAMINATION

The usual varnish examination includes the determination of specific gravity, flash point, acid number, amount and nature of the thinner, amount and nature of the ash, a qualitative test for rosin, a drying test on glass, a panel test, in which the drying and rubbing properties and the action of hot and cold water are noted;

¹ In this paper the term "oil varnish" means varnish containing oil and resin. "Short-oil" varnish contains considerable more resin than oil and "long-oil" varnish considerable more oil than resin.

² "German and American Varnish Making," M. Bottler and A. H. Sabin (1912).

³ "German and American Varnish Making," M. Bottler and A. H. Sabin (1912); "The Technology of Paint and Varnish," A. H. Sabin (1904); "The Chemistry of Paint," M. Toch (1907); "The Manufacture of Varnish and Kindred Industries," A. Livache and J. G. McIntosh (1908).

and observation of the consistency and color. In general, such an examination has only a limited value. That a varnish is of poor quality can be determined by these tests, but the superiority of one sample over another when both are of good quality can not be so ascertained, and exposure tests which may require months are then necessary. The only satisfactory method for testing varnishes which are to be used for fine work, such as the varnishing of expensive furniture, is to have the samples tried out by an expert operator skilled in such work. At present, however, neither the practical varnisher nor the chemist can determine by tests the wearing qualities of a sample.

There is a probability that with improved methods of varnish analysis and with the aid of exposure tests on analyzed samples, characteristics may be discovered which will show the relative wearing qualities of samples. With this in view the development of a method for the determination of oil and resin is desirable. The identification of the various resins is a more difficult problem, the possibilities of which are not very promising.

IV. THE DETERMINATION OF OIL AND RESIN

1. GENERAL

The various methods that have been proposed for the estimation of oil and resin may be classified as follows:

Calculation of the oil content from the determined glycerol yield; separation by the use of solvents; and esterification methods, some of which include separation by petroleum ether. Details of these methods will be given in connection with the study of them.

2. PREPARATION OF VARNISHES OF KNOWN COMPOSITION

As previously noted, it seemed especially desirable to test such methods with samples of known composition and history. Accordingly, samples were prepared under conditions which permitted the desired data to be obtained.

Since in the preparation of oil varnish losses occur from both the oil and the resin, to calculate the composition of the varnish it is necessary to assume a certain loss for one or the other, the mag-

nitude of the same depending upon the conditions of manufacture. To determine the loss that occurs when linseed oil is heated and to ascertain whether losses occur from oil and resin when the two are heated together, which are greater than when the two are heated separately, the following experiments were made:

EXPERIMENT 1.—300 g of linseed oil were heated in a beaker at 300° C and the loss in weight noted.

EXPERIMENT 2.—Samples of various resins were heated over a Bunsen burner until completely melted. Samples of melted resin, of linseed oil, and mixtures of approximately equal parts of the two were heated under the same conditions and the losses in weight noted. The results, as given in Table 1, show that under the conditions of manufacture of the special varnishes (see Table 2) losses of from less than 1 per cent to 3 per cent may be assumed to occur in the weight of the oil, and that the calculated losses in weight from the oil-resin mixtures are approximately the same as those obtained by experiment. It has been shown ⁴ that Chinese wood oil when heated for half an hour at 300° C loses 0.5 per cent in weight. The losses which occur when oils are heated depend not only upon the time and temperature, but also upon the size and shape of the vessel and the amount of exposed surface, so that in estimating the losses in weight occurring during the manufacture, and thereby the oil and resin contents of the finished varnishes, it is to be expected that the figures will be only approximately correct. However, such approximation is all that can be expected in the control of the composition of oil varnish during manufacture.

Four samples of varnish were prepared in the factory.⁵ These will be designated in this paper as varnishes A, B, C, and D. Three additional samples were prepared in the laboratory, using other resins than those in varnishes A, B, C, and D. These samples will be designated later as varnishes E, F, and G. Data regarding the constituents and preparation of these samples are shown in Table 2.

⁴ Boughton, *Proc. Amer. Soc. for Test. Mat.*, 14, II, 252 (1914).

⁵ For the opportunity to prepare these samples and for assistance and advice the writer is indebted to L. P. Nemzek and John Lucas & Co. (Inc.).

TABLE 1

Losses in Weight on Heating Oils, Resins, and Oil-Resin Mixtures

Experiment.	Material.	Time of heating	Temperature	Loss in weight.	
				Determined	Calculated
		Minutes	°C	Per cent	Per cent
1.....	Linseed oil.....	60	300	1.7
	Do.....	120	300	2.7
2.....	Linseed oil.....	45	250-275	1.9
	Kauri.....	45	250-275	6.9
	Linseed oil, 47 per cent; kauri, 53 per cent....	45	250-275	3.9	4.5
	Linseed oil.....	45	250-275	2.2
	Manila.....	45	250-275	3.7
	Linseed oil, 47 per cent; manila, 53 per cent..	45	250-275	3.7	3.0
	Linseed oil.....	45	250-275	2.2
	Zanzibar.....	45	250-275	2.9
	Linseed oil, 48 per cent; Zanzibar, 52 per cent.	45	250-275	2.9	2.6
	Linseed oil.....	45	250-275	1.9
	Pontianak.....	45	250-275	4.3
	Linseed oil, 51 per cent; Pontianak, 49 per cent	45	250-275	3.9	3.1

The composition of each of the finished varnishes was calculated as follows: By deducting from 100 per cent the percentages of ash and thinner, as determined by the usual methods, the sum of the oil and resin contents was obtained. The percentage of oil present was calculated from the amount added, correcting for the estimated losses in weight as shown in Table 2. The percentage of resin was found by difference. The composition of the samples is given in Table 3.

Owing to the approximate nature of the corrections applied for losses in weight of the oils, there may be considerable error in the first decimal place of the figures. The samples analyzed were filtered varnishes, but an examination of the unfiltered varnishes showed amounts of sediment that were too small to cause appreciable errors in the calculations. Further examination of varnishes A, B, C, and D by the usual methods gave the results shown in Table 4.

TABLE 2

Data on Preparation of Special Varnishes

Sample	Constituents	Time of heating ^a	Maximum temperature ^a	Estimated loss in weight	
				Oil	Resin ^b
		Minutes	° C	Per cent (c)	Per cent
A.....	Rosin, linseed oil, lime, sugar of lead, and benzene.	15	265		8
B.....	Rosin, linseed oil, Chinese wood oil, lime, litharge, manganese borate, and benzene.	45	300	2	20
C.....	Bold Zanzibar, Sierra Leone copal, borate oil, ^d turpentine, and Damar varnish.	(e)	(c)	20
D.....	Bold Zanzibar, kauri, borate oil ^d and turpentine.	180	290	3	22
E.....	Manila, linseed oil, litharge, manganese dioxide, and turpentine.	45	260	2	25
F.....	Congo, linseed oil, litharge, manganese dioxide, and turpentine.	45	260	2	35
G.....	Pontianak, linseed oil, litharge, manganese dioxide, and turpentine.	45	260	2	28

^a After addition of the oil.^b Includes loss occurring before addition of oil.^c Less than 1 per cent.^d Linseed oil, containing manganese borate.^e Allowed to cool after addition of oil.

TABLE 3

Composition of Special Varnishes

Varnish	Ash (determined)	Volatile thinner (determined)	Oil (calculated)	Resin (calculated)
	Per cent	Per cent	Per cent	Per cent
A.....	3.9	43.6	3.9	48.6
B.....	2.4	53.2	31.9	12.5
C.....	.2	54.0	16.1	29.7
D.....	.1	47.5	36.1	16.3
E.....	.04	50.6	26.2	23.2
F.....	.9	48.0	36.1	15.0
G.....	.8	50.1	27.6	21.5

TABLE 4

Miscellaneous Data on Special Varnishes

Varnish	Color	Odor	Viscosity (relative)	Acid number	Qualitative test for rosin	
					Color (Lie- bermann & Storch)	Color (Halphen Hicks ^a)
A.....	Medium..	Mineral oil....	Seconds 6	49.7	Bluish purple..	Blue to blu- ish purple.
B.....	Dark.....do.....	13	8.6	Purple; more reddish than A.	Do.
C.....	Light.....	Turpentine....	40	8.1	Brown.....	Yellow.
D.....	Dark.....do.....	10	5.1do.....	Faint red-pur- ple.

^a Using phenol and bromine (J. Ind. Eng. Chem., 3, p. 86, (1911).

3. STUDY OF METHODS

(a) DETERMINATION OF THE GLYCEROL YIELD WITH SUBSEQUENT CALCULATION OF THE OIL CONTENT.—Lewkowitsch ⁶ stated that the "boiled oil" content of a varnish can be calculated from the glycerol yield, but gives no figures or references. In order to determine the factor for calculating the oil content of a sample from the glycerol yield the latter was determined with samples of oil by the following method. (Method 1, Table 5.) Four to 5 g of oil were saponified in a beaker with alcoholic potash and after evaporating to a sirupy consistency on the steam bath, water was added, and the solution again evaporated. This was repeated and then about 100 cc of water were added. After the soap was dissolved the fatty acids were liberated with dilute sulphuric acid, a piece of paraffin was added, and the mixture heated on the steam bath for about 10 minutes with stirring. The beaker was cooled and after the fatty acids-paraffin layer had solidified the aqueous solution was decanted through a folded filter into a 300 cc graduated flask. The mass of paraffin and fatty acids was treated with 50 cc of hot water and stirred for a few minutes on the steam bath. The cooling and decantation were repeated and a second washing was made in the same way. A little silver

⁶ Chem. Tech. and Anal. of Oils, Fats, and Waxes, 5th ed., III, p. 164 (1915).

sulphate was added and the solution diluted to 300 cc and shaken. The contents were then filtered and 200 cc of the clear filtrate were used for the determination of glycerol by the bichromate method. It is evident from the results recorded under experiments 1 and 2, Table 5, that the glycerol yield will vary according to the amount of heating that linseed oil has undergone and will be approximately 10 per cent. When determinations of the glycerol yields of varnishes A to D were made by this method very erratic results were obtained, most of which, except with varnish B, were higher than those calculated by dividing the oil content by 10. The method was modified so that the beakers containing the soap solution were heated overnight on a steam-heated hot plate and in an air bath at 90° C, but still good results were not obtained. Saponification with 10 per cent aqueous potassium-hydroxide solution was then tried. (Method 2, Table 5.) The saponifications were made in pressure bottles which were heated in a steam bath. The procedure subsequent to the addition of sulphuric acid was the same as is given above. From the results shown in Table 5 it is evident that the use of the factor 10 gives fairly accurate results for oil content of the varnishes except with varnish B, which contained Chinese wood oil. Why the presence of this oil should have such an effect, even though the samples of Chinese wood oils examined showed glycerol yields of approximately 10 per cent, was not ascertained. The difficulty may be due to incomplete saponification, since, according to Ware and Schumann,⁷ polymerized Chinese wood oil is not readily saponified. In some of the determinations with varnish B, however, saponification was continued for 20 hours. The calculation from the glycerol yield of the oil content of a varnish containing Chinese wood oil is, therefore, not justified.

(b) SEPARATION BY THE USE OF SOLVENTS.—Scott⁸ devised a method for the separation of oil and resin by treatment with cold petroleum ether, which is quoted by Holley⁹ without comment. Darner¹⁰ stated that Scott's method is not reliable.

⁷ J. Ind. Eng. Chem., 7, p. 571 (1915).

⁸ Drugs, Oils, and Paints, 15, pp. 132, 219 (1900).

⁹ Analysis of Paint and Varnish Products, p. 260 (1912).

¹⁰ North Dak. Agric. Expt. Sta. Paint Bull., 1, No. 6 (1915).

TABLE 5
Glycerol Yields and Calculated Oil Contents

Experiment	Material	Method	Glycerol yield	Glycerol yield X 10	Oil present
			Per cent	Per cent	Per cent
1.....	Raw linseed oil.....	1	11.14 11.10	111.4 111.0	
Average.....			11.12	111.2	100.00
2.....	Same oil, after being heated two hours at 275° C.	1	9.62 9.72	96.2 97.2	
Average.....			9.67	96.7	100.00
3.....	Same as in experiment No. 2.....	2	9.73 9.67	97.3 96.7	
Average.....			9.70	97.0	100.00
4.....	Chinese wood oil.....	2	10.61 10.63	106.1 106.3	
Average.....			10.62	106.2	100.00
5.....	Same oil, after being heated two hours at 170° C.	2	10.08 10.15	100.8 101.5	
Average.....			10.12	101.2	100.00
6.....	Chinese wood oil used in making varnish B...	2	10.42	104.2	100.00
7.....	Varnish A.....	2	0.42 0.53 0.51	4.2 5.3 5.1	
Average.....			0.49	4.9	3.9
8.....	Varnish B.....	2	2.40 1.71 1.82 2.31 2.50 2.56	24.0 17.1 18.2 23.1 25.0 25.6	
Average.....			^a 2.53	^a 25.3	31.9
9.....	Varnish C.....	2	1.77 1.76	17.7 17.6	
Average.....			1.77	17.7	16.3

^a Average of last two determinations.

TABLE 5—Continued

Glycerol Yields and Calculated Oil Contents—Continued

Experiment	Material	Method	Glycerol yield	Glycerol yield $\times 10$	Oil present
			Per cent	Per cent	Per cent
10.....	Varnish D.....	2	3.66	36.6	
			3.38	33.8	
			3.41	34.1	
			3.38	33.8	
			3.57	35.7	
Average.....			3.48	34.8	36.1
11.....	Mix ready for thinning, taken during manufacture of varnish B.	2	5.43	54.3	73

Bochand and Gillet ¹¹ outlined a scheme for varnish analysis in which they endeavored to separate oil and resin by the Gladding method, as modified by Hübl and Stadtler, based on the difference in solubility of the silver salts. Their results were unsatisfactory, only 19.5 per cent of oil being obtained from a sample containing 25 per cent. Lewkowitsch ¹² has shown that the Gladding method and modifications thereof do not give reliable results. In the present investigation no tests were made on this method.

Livache and McIntosh ¹³ stated that the simplest and most exact method for the determination of oil and resin is to treat a dried film with an appropriate solvent, the weight of oil being calculated from the weight of insoluble linoxyn, allowing for an absorption of 15 to 16 per cent of oxygen by the linseed oil.

A method was devised by Voorhees,¹⁴ which is as follows: The varnish is treated with a small amount of chloroform and a large amount of petroleum ether, the precipitate is separated and weighed. The petroleum ether solution is evaporated to dryness, and the residue is oxidized by heating for eight days at 100° C and is then extracted with chloroform. The precipitate is called "hard gums," and the chloroform extract after oxidation is

¹¹ Proc. Eighth Intern. Cong. Applied Chem., 12, pp. 7-12 (1912).

¹² Oils, Fats, and Waxes, 5th ed., I, p. 625 (1913).

¹³ Manufacture of Varnishes and Kindred Industries, II, p. 183 (1908).

¹⁴ This method was published in Bull. 109, Bureau of Chemistry, Dept. of Agr., but was omitted from revised edition.

assumed to be "gums soluble in petroleum ether." The part insoluble in chloroform is assumed to be oxidized oil.

Of the above methods, that of Voorhees appeared to be the most promising. Preliminary analyses¹⁵ of varnishes A to D by this method yielded results which were not in accord with the calculated composition. Tests were then made on each step of the method. In some experiments the varnish was treated with a mixture of 2 cc of chloroform and 75 cc of petroleum ether¹⁶ (method 1, Table 6), and in others with petroleum ether alone (method 2, Table 6), the precipitates in each case being analyzed by the esterification method, outlined later on page 23, and the results corrected as indicated on page 26. The results obtained are shown in Table 6. Although the amount of precipitate analyzed was so small that the results are only approximate, it is evident that much oil is precipitated with the resin, especially in the presence of Chinese wood oil. These results indicate that the same precipitation of oil would occur in any method which involves direct treatment of a varnish with petroleum ether.

To determine the accuracy of the last step in Voorhees's method, i. e., the extraction of the oxidized film with chloroform to remove the gums, the following experiments were made. The petroleum ether-chloroform solutions obtained in experiments 1 and 2, Table 6, after separation of the precipitates, were flowed on strips of filter paper, which were then placed in an air bath and heated for eight days at 100–110° C. They were then extracted with chloroform at the boiling point. The amounts of extracts obtained, calculated as percentages of the varnishes, are shown in Table 7, experiments 1 and 2.

Some experiments were made on the extraction of films of oxidized oils and varnishes, omitting the treatment with petroleum ether (method of Livache and McIntosh). One g samples of heated linseed oil and Chinese wood oil were dissolved in chloroform and the solution was flowed on filter paper. The sheets were heated for seven days at 100–110° C in an air bath and then extracted with chloroform at the boiling point. Samples of varnishes A to D were similarly treated. Further extrac-

¹⁵ Analyses by F. A. Wertz.

¹⁶ The portion distilling between 40–65° C.

tion with benzene of the film of varnish D yielded an additional extract of only 0.5 per cent. To determine whether the resin could be extracted with chloroform from a film produced by oxidizing the fatty and resin acids, samples of varnishes C and D were saponified in shallow dishes, the acids were liberated by the addition of hydrochloric acid, and the mixture evaporated to a pasty consistency and mixed with sand. The dishes were heated on a steam-heated hot plate for eight days, and the mass was then extracted with chloroform at the boiling point. It is evident from all the results shown in Table 7 that, except with varnish A, which contained 48 per cent of rosin, only a portion of the resinous matter present was extracted. As methods of analysis, neither that of Voorhees nor that of Livache and McIntosh appears reliable.

TABLE 6

Amounts and Composition of Precipitates Obtained By Voorhees' Method

Experiment	Varnish	Method	Precipitate	Composition of precipitates			
				Resin		Oil	Ash
				Resin acids + unsaponifiable matter	By difference		
			Per cent	Per cent	Per cent	Per cent	Per cent
1.....	C.....	1	18.9	65	71	29
2.....	D.....	1	7.2	50	54	46
3.....	B.....	2	25.3	^a 28	^a 24	68	8
4.....	C.....	2	23.5	65	69	31
5.....	D.....	2	8.5	54	^b 46
6.....	H ^c	2	21.8	49	55	41	4

^a Rosin. ^b By difference. ^c A mixture of varnishes B and C containing 10 per cent of Chinese wood oil.

TABLE 7
Extraction of Oxidized Films

Experiment	Material	Time of oxidation	Time of extraction	Extract	Resin present
		Days ^a	Hours	Per cent	Per cent
1.....	Portion of varnish C soluble in petroleum ether; CHCl ₃ mixture.	8	6	5.9	^b 16
2.....	Portion of varnish D soluble in petroleum ether; CHCl ₃ mixture.	8	6	7.7	^b 13
3.....	Heated linseed oil.....	7	3	3.5 4.5	
Av.....				4.0	None.
4.....	Heated Chinese wood oil.....	7	3	1.7 2.3	
Av.....				2.0	None.
5.....	Varnish A.....	6	6	53.3	
		7	6	53.8	48.6
6.....	Varnish B.....	6	3	6.3	
		6	6	6.6	
		7	3	5.4	
		7	6	5.5	12.5
7.....	Varnish C.....	6	3	13.1	
		6	6	13.1	
		7	3	10.3	
		7	6	10.5	29.7
8.....	Varnish D.....	1	3	12.6	
		1	6	13.6	
		2	3	9.8	
		2	6	10.3	
		4	3	6.6	
		4	6	7.1	
		6	3	6.4	
		6	6	6.8	
		7	3	5.2	
		7	6	5.3	16.3
9.....	Fatty acids, resin acids, and unsaponifiable matter of varnish C.	8	6	^c 11.2	^c 29.7
10.....	Fatty acids, resin acids, and unsaponifiable matter of varnish D.	8	6	^c 3.9	^c 16.3

^a One day=24 hours.^b Total resin in varnish minus resin precipitated by petroleum ether.^c Per cent of varnish.

(c) ESTERIFICATION METHODS.—The methods most commonly used for the separation of fatty oil and rosin are those based upon the fact that in the presence of a dehydrating agent fatty acids and ethyl alcohol react to form esters, while rosin acids do not.

In Twitchell's¹⁷ method dry hydrochloric-acid gas is passed through a solution of the mixed acids in absolute ethyl alcohol. In Wolff's¹⁸ method a mixture of concentrated sulphuric acid and a solution of the mixed acids in absolute ethyl or methyl alcohol is boiled for two minutes. In both methods the subsequent procedure is as follows:

The mixture of fatty acid esters and rosin acids is dissolved in petroleum ether. The rosin acids are separated by treatment with a solution of potassium hydroxide and subsequently liberated and weighed, or an alcoholic solution of the fatty acid esters and rosin acids is titrated with standard alkali, the amount of rosin present being calculated by assuming that 1 cc of normal alkali equals 0.346 g of rosin. When this method is used for the analysis of varnishes which contain resins that yield material insoluble in petroleum ether, the insoluble matter must be separated. Also, if appreciable amounts of resin (other than rosin) remain dissolved in the petroleum ether, the volumetric method can not be used, since the various resins have different neutralization values.¹⁹

In attempting to determine rosin in Kauri varnish, Gill²⁰ saponified the nonvolatile portion with alcoholic potash and liberated the fatty and resin acids together. He then separated the fatty acids from the resin acids by the Twitchell method. He gave no figures to show the accuracy of the separation by this method.

Holley²¹ published a method of varnish analysis which includes the separation of oil and resin by the Twitchell method, but gave no figures to show the accuracy of the results. The amount of resin present was assumed to be equal to the weight of the resin acids obtained, and, since this is approximately true only with rosin and not with other resins, the method, as described, can not be considered reliable.

Lewkowitsch²² obtained low yields of what he called "gum resin" on treating copal and mastic by the Twitchell method and considered the latter useless for varnish analysis.

¹⁷ J. Soc. Chem. Ind., 10, p. 884 (1891).

¹⁸ Chem. Ztg., 38, pp. 369-370, 382-383, 430 (1914).

¹⁹ See table in Lewkowitsch, Chem. Tech. of Oils, Fats, and Waxes. 5th ed., III, p. 165 (1915).

²⁰ J. Amer. Chem. Soc., 28, p. 1723 (1906).

²¹ Analysis of Paint and Varnish Products, p. 259 (1912).

²² Oils, Fats, and Waxes, 4th ed., III, p. 127 (1909).

McIlhiney²³ stated that the oil and resin in a varnish can not be separated directly by any solvent, and devised a method (for the separation of oil, rosin, and "hard gums") in which the varnish is saponified with alcoholic potash, the alcohol distilled off, and absolute alcohol is added to the residue. The saponification number is determined by titrating the excess of alkali with a solution of acetic acid in absolute alcohol. The fatty and resin acids are then liberated by adding the calculated amount of acetic acid solution. Petroleum ether is added and then water, producing a precipitate which McIlhiney terms "hard gum." The fatty and rosin acids remaining dissolved in the petroleum ether are subsequently separated by the Twitchell method. If fatty acids from oxidized oil are precipitated with the "hard gum," they are separated by treating the precipitate with 85 per cent alcohol. No results by this method are recorded. Lewkowitsch²⁴ stated that McIlhiney's method "can only lead to approximate results." Darner,²⁵ in using McIlhiney's method with a varnish containing 31.8 per cent of oil, obtained 38.1 per cent. He erroneously stated that McIlhiney recommends the use of *absolute* alcohol for the removal of oxidized fatty acids from the precipitated gum. Darner stated that in McIlhiney's method Chinese wood oil, if present, will be precipitated with the gum, and also that the manipulation of the method is difficult, the separation of the precipitated gum being very troublesome. The same difficulty has been noted by the author.

Darner devised the following method:

Three to four grams of varnish are spread out on an Adams filter coil which has been dried and weighed along with an extraction thimble. The coils absorb water rapidly and for this reason the coils and thimble must be weighed in a weighing bottle. The varnish is best weighed and added to the coil from a dropping bottle. The coil is then held in the mouth of a 300 cc weighed Erlenmeyer flask, and 100 cc of petroleum ether, 0.670 sp. gr., added slowly. A large percentage of the varnish will be washed out of the coil by this treatment. The coil is then placed in the extraction thimble and extracted for 36 hours or until extraction is complete; 150 cc of petroleum ether, 0.670 sp. gr., is added to the flask and the flask cooled to 3° C, until the gums settle and the liquid is clear. The liquid containing the oils and rosin is poured off the gums and the flask washed several times with petroleum ether and the washings added to the original

²³ Proc. Amer. Soc. for Test. Mat., 8, p. 596 (1908).

²⁴ Chem. Tech. Oils, Fats, and Waxes, 5th ed., III, p. 166 (1915).

²⁵ N. Dak. Agr. Expt. Sta. Paint Bull., 1, No. 6 (1915).

petroleum-ether extract. The Erlenmeyer flask and thimble are then dried at 105°C to constant weight. The increase in weight of the flask and thimble minus the weight of the metallic driers represents the weight of hard gums in the varnish. The extract from the gums is freed of the petroleum ether, saponified with $\frac{1}{2}\text{N}$ alcoholic potash and the unsaponifiable matter extracted with ether. The rosin and fatty acids are then released with $\frac{1}{2}\text{N}$ hydrochloric acid and extracted with ether. The acids are then freed of the ether and the rosin determined by Twitchell's method.

With 13 samples of varnish Darner obtained remarkably accurate results for oil, rosin, and gum. He does not state whether the rosin was determined gravimetrically or volumetrically. He records the figures representing the amounts of oil, rosin, and gum (estimated and found) to hundredths of 1 per cent. In view of what has been said regarding the impossibility of ascertaining exactly how much the oil and resin, respectively, lose in weight during manufacture, this does not appear justifiable.

Preliminary to the study of the esterification methods the following experiments were made. The yields of fatty acids and of unsaponifiable matter²⁶ from raw linseed oil and from the same oil after heating for one hour at 275°C were determined. The results, as given in Table 8, show that to calculate the amount of oil from the fatty acid yield of a varnish, the factor 1.06 should be used, which, for the purpose of varnish analysis, is not materially different from that obtained with raw linseed oil, 1.07.

TABLE 8

Yields of Fatty Acids and Unsaponifiable Matter from Linseed Oil

Material	Unsaponifiable matter	Fatty acids
	Per cent	Per cent
Raw linseed oil.....	1.3	92.8
	1.2	93.1
Average.....	1.25	92.95
Same oil after heating 1 hour at 275°C	1.1	94.0
	1.1	94.2
Average.....	1.1	94.1

²⁶ The term "unsaponifiable matter," as used in the experimental part of this paper, means the material extracted by ether after saponification with alcoholic potash, the ether solution being subsequently washed with water. In the analyses of varnishes the amounts of resin acids and unsaponifiable matter obtained frequently varied greatly with the same sample, so that, while the sum of the two serves as a check on the amount of resin present, the ratio of the two has practically no significance.

The Wolff method for the separation of oil and rosin is shorter and simpler than the Twitchell method. The two methods were compared first with fatty acids prepared from raw linseed oil, the solution of the esters and unesterified acids being titrated with standard alkali and the results calculated as "acid number" (milligrams of potassium hydroxide per gram of fatty acids taken). The acid (neutralization) value of linseed-oil fatty acids is 196-199, so that the results given in Table 9, experiment 1, show that by the Twitchell method 98.5 per cent of the fatty acids was esterified and by the Wolff 96.9 per cent. The two methods were further compared by analyses of a mixture of rosin and linseed oil and of the nonvolatile portion of varnish D, using ether as solvent after esterification and determining the resin acids gravimetrically. For the purposes of varnish analysis the two methods are in substantial agreement. (See Table 9 (2).) The reason for the excessive percentage of oil obtained in the analysis of the nonvolatile portion of varnish D will be mentioned later.

TABLE 9

Results by Twitchell and Wolff Methods

(1) ESTERIFICATION OF LINSEED OIL FATTY ACIDS AND SUBSEQUENT TITRATION

Material	Method	Acid number after esterification
Raw linseed oil fatty acids.....	Twitchell.....	2.7
		3.3
	Average.....	3.0
	Wolff ^a	6.6
		5.7
	Average.....	6.15

^a Sometime after the completion of the experimental work of this paper an experiment was made on the esterification of linseed oil fatty acids by Wolff's method, using absolute methyl alcohol. An average acid number of 4.1 was obtained.

(2) ESTERIFICATION AND GRAVIMETRIC DETERMINATION OF OIL AND RESIN IN MIXTURES

Material and method	Fatty acids	Oil		Resin		
		Present	Found	Present	Found	
					By difference	Resin acids + unsapon. matter ^a
Linseed oil and rosin:	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Twitchell.....	48.0		51.4		48.6	47.4
	48.2		51.6		48.4	47.0
Average.....	48.1	51.6	51.5	48.4	48.5	47.2
Wolff.....	49.6		53.1		46.9	45.6
	49.7		53.2		46.8	47.0
Average.....	49.65	51.6	^b 53.15	48.4	46.85	46.3
Nonvolatile portion of varnish D:						
Twitchell.....	66.5		70.5		29.5	29.6
	67.6		71.7		28.3	28.9
Average.....	67.05	69	^c 71.1	31	28.9	29.25
Wolff.....	66.9		70.8		29.2	28.5
	67.7		71.8		28.2	27.6
Average.....	67.3	69	^c 71.3	31	28.7	28.05

^a Corrected for unsaponifiable matter in oil.^b Fatty acids $\times 1.07$.^c Fatty acids $\times 1.06$.

McIlhiney's method was used for the analysis of varnishes C and D, and gave the results shown in Table 10. As neither of these samples contained rosin, whereas the amounts of resin acids ²⁷ obtained from the petroleum ether ²⁸ solution were 5 and 4.8 per cent, respectively, it is evident that as a method for the separation of "hard gum" from rosin the procedure is not reliable. The result for total oil in C is too high and in D is too low. If the treatment with 85 per cent alcohol to remove the oxidized fatty acids from the "hard gums" had been omitted in the analysis of C, the results for total oil and total resin would have been fairly close to the amounts actually present. On samples of unknown composition, however, one can not tell whether this step should be included. The analysis of the material insoluble in petroleum

²⁷ Determined gravimetrically.²⁸ The portion distilling between 40-65° C.

ether, the results of which are shown in Table 11, was made by the method outlined later on page 23, applying the correction mentioned on page 26. Owing to the small amount of material analyzed and the approximate nature of the correction, the figures obtained must be considered as approximations, but it is clearly shown that much less oil (fatty acids) is precipitated with the resin than in Voorhees's method (see p. 12), in which the preliminary saponification and liberation of the fatty and resin acids are omitted.

TABLE 10
Results with McIlhiney's Method

Experiment	Varnish	Oil			
		Present	Found		
			Fatty acids soluble in petroleum ether x 1.06	Fatty acids insoluble in petroleum ether and soluble in 85 per cent alcohol x 1.06	Total oil
		Per cent	Per cent	Per cent	Per cent
1.....	C.....	16.1	15.3	3.8	19.1
2.....	D.....	36.1	27.9	2.3	30.2

Experiment	Varnish	Resin					
		Present	Found				Total resin by difference
			Insoluble in petroleum ether and in 85 per cent alcohol	Soluble in petroleum ether		Total resin	
Resin acids	Unsat- urizable matter						
		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1.....	C.....	29.7	14.0	5.0	7.2	26.2	26.7
2.....	D.....	16.3	12.8	4.8	5.2	22.8	22.2

TABLE 11
Results of Analysis of Matter Insoluble in Petroleum Ether (Varnish C)

	Per cent.
Total precipitate was 18.2 per cent of varnish.	
{ Fatty acids.....	7
{ Resin, by difference.....	93
{ Resin (resin acids plus unsaponifiable matter).....	87

TABLE 12

Results of Analysis of Varnish by Darner's Method

Experiment	Material	Oil		Resin					
		Present	Found fatty acids $\times 1.06$	Present	Found				
					Insoluble in petro- leum ether	Soluble in petro- leum ether		Total resin	Total resin by differ- ence
						Resin acids	Unsa- ponifiable matter		
		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1.....	C.....	16.1	16.3	29.7	15.1	4.4	10.3	29.8	29.5
2.....	D.....	36.1	32.2	16.3	13.1	4.2	4.2	21.5	20.2
3.....	E.....	26.2	20.2	23.2	16.4	5.9	5.9	28.2	29.2
4.....	Sierra Leone								
	Copal.....	0.0	1.9	100.0	92.6	1.9	3.5	98.0	98.1
5.....	Pontianac.....	0.0	0.4	100.0	91.0	4.2	1.8	97.0	99.6

Darner's method was used for the analysis of varnishes C, D, and E, the resin acids from the petroleum-ether²⁹ solution being determined gravimetrically. None of these samples contained rosin. The results as given in Table 12 show that with the "short oil" varnish, C, the results for total resin and total oil are very satisfactory, but for the "long oil" varnish, D, and varnish E, the results for oil content are too low. Also, in all these analyses, appreciable amounts of resin acids were obtained from the petroleum-ether solution, which indicates that the method, as a means for accurate separation of "gum" and rosin, is not reliable.

Samples of two resins, Sierra Leone Copal, and Pontianac, were melted to complete fusion, and 2 g portions were analyzed by Darner's method. The results as given in Table 12 show that considerable resin remains dissolved in the petroleum ether, which in a varnish analysis by this method would not be weighed as "gum."

Since the use of petroleum ether in esterification methods gave results for oil contents, which, with "long oil" varnishes, were low, the following method, including esterification by the Wolff method and the use of ethyl ether instead of petroleum ether, was

²⁹ The portion distilling between 55-80°C. Sp. gr. at 15.6/15.6°C.=0.671.

used for the analysis of varnishes A to G. Approximately 4 g of varnish were placed in a flask and about 25 cc of water added. The mixture was boiled until the volume of the water was about 10 cc, thus removing the volatile thinner. Alcoholic potash and benzene were added and the flask placed on the steam bath for one hour. The unsaponifiable matter was partially removed by one extraction with ether. After hydrochloric acid had been added, the fatty acids, resin acids, and remaining unsaponifiable matter were dissolved in ether and were recovered from the ether solution and dried. They were then treated with absolute ethyl alcohol and sulphuric acid. After dilution with 10 per cent sodium-chloride solution, the resin acids, fatty acid esters, and unsaponifiable matter were extracted with ether and the resin acids removed by treatment with a solution of potassium hydroxide. Hydrochloric acid was added to the resin soap solution and the resin acids extracted by ether. After washing the ether with water the resin acids were recovered, dried at 110°C and weighed. The fatty acid esters and unsaponifiable matter were recovered from the ether solution and were treated with alcoholic potash. The unsaponifiable matter was removed by repeated extractions with ether. The united ether solutions were washed with water and added to the ether solution of unsaponifiable matter previously obtained. The ether was distilled off and the unsaponifiable matter dried at 110°C and weighed. The solution of the soaps of the fatty acids was treated with hydrochloric acid, the fatty acids were dissolved in ether and, after the ether solution had been washed with water, were recovered, dried at 110°C , and weighed. It had been found by preliminary experiments that it is almost impossible to remove all the unsaponifiable matter previous to esterification. It was also found that heating the fatty acids from linseed oil for one hour in air at 110°C caused a gain in weight of only 0.3 per cent. The lack of concordance in duplicate analyses being so much greater than this, heating in carbon dioxide was omitted.

The results are shown in Table 13. With varnish A the results are satisfactorily accurate. With varnish B the results for resin content are somewhat too high. With varnishes C to G, which

contained resins other than colophony, the results for resin contents are too low, showing that the material weighed as fatty acids must have contained some resinous matter. With the possible exception of varnish B, the results for resin contents obtained by adding the percentages of resin acids and unsaponifiable matter are in fair agreement with those obtained by estimating the resin by difference. That the removal of nearly all of the unsaponifiable matter before esterification does not prevent the contamination of the fatty acids with resinous matter is shown by the results recorded under experiment 8, Table 13, in which the soap solution after the first saponification was extracted four times with ether.

TABLE 13
Analysis of Varnishes

Experiment	Varnish	Fatty acids	Resin acids	Unsaponifiable matter	Oil		Resin		
					Present	Found, fatty acids $\times 1.06$	Present	Found	
								Unsaponifiable matter + resin acids	By difference
		Per ct	Per ct	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1.....	A	4.4	34.8	12.0	3.9	4.7	48.6	46.8	47.8
		4.6	35.2	12.6		4.9		47.8	47.6
Av.....		4.5	35.0	12.3		4.8		47.3	47.7
2.....	B	28.5	10.7	3.3	31.9	30.2	12.5	14.0	14.2
		28.3	7.9	8.4		30.0		16.3	14.4
		29.8	6.0	7.9		31.6		13.9	12.8
		30.2	9.1	4.3	16.1	32.0	29.7	13.4	12.4
Av.....		29.2	8.4	6.0		31.0		14.4	13.4
3.....	C	17.8	13.8	12.2	19.1	18.9	26.9	26.0	26.9
		17.5	13.5	15.2		18.6		28.7	27.2
		19.8	13.1	12.3		21.0		25.4	24.8
		16.8	10.9	16.9	12.6	17.8	27.2	27.8	28.0
		17.9	14.0	11.9		19.0		25.9	26.8
		13.9	13.3			27.4
		12.6	14.8	18.0	26.9
Av.....		18.0	13.1	13.8		19.1		26.9	26.7

TABLE 13—Continued
Analysis of Varnishes—Continued

Experiment	Varnish	Fatty acids	Resin acids	Unsa- poni- fiable matter	Oil		Resin		
					Present	Found, fatty acids \times 1.06	Present	Found	
								Unsapon- ifiable matter + resin acids	By dif- ference
		Per ct	Per ct	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
4.....	D	35.1	3.9	13.0	36.1	37.2	16.3	16.9	15.0
		33.4	4.6	12.3		35.4		16.9	16.8
		36.6	5.3	8.9		38.8		14.2	13.4
		34.6	4.5	11.4		36.7		15.9	15.5
		35.0	4.6	10.3		37.1		14.9	15.1
Av.....		34.9	4.6	11.2		37.0		15.7	15.2
5.....	E	25.8	13.3	7.5	26.2	27.9	23.2	20.8	21.5
		24.8	13.6	6.9		26.9		20.5	22.5
		25.3	13.5	7.2		27.4		20.7	22.0
Av.....		25.3	13.5	7.2		27.4		20.7	22.0
6.....	F	35.8	3.0	10.9	36.1	37.9	15.0	13.9	13.2
		34.9	3.3	8.3		37.0		12.6	14.1
		35.4	3.2	9.6		37.5		13.3	13.7
Av.....		35.4	3.2	9.6		37.5		13.3	13.7
7.....	G	27.4	11.6	7.0	27.6	29.0	21.5	18.6	20.1
		27.8	11.5	7.5		29.5		19.0	19.6
		27.6	11.6	7.3		29.3		18.8	19.9
Av.....		27.6	11.6	7.3		29.3		18.8	19.9
8.....	C ^a	17.4	14.2	12.9	16.1	18.3	29.7	27.1	27.5
		17.1	13.8	12.2		18.1		26.0	27.7
		17.3	14.0	12.6		18.2		26.6	27.6
Av.....		17.3	14.0	12.6		18.2		26.6	27.6

^a Modified method.

To determine the existence and magnitude of errors due to the contamination of the fatty acids with resinous matter, the products obtained by heating various resins at about 300° C were analyzed by the method. Samples of the melted resins taken during the manufacture of varnishes C and D were also analyzed. The yields of material which in a varnish analysis would be weighed as "fatty acids," as shown in Table 14, varied from 3.1 to 10.6 per cent. Were there no other error in the method it

would appear safe to assume that if the yields of resin obtained be multiplied by 1.07, results that are correct to within 5 per cent of the amounts present would be obtained. The average results obtained with varnishes C to G, when thus corrected, are shown in Table 15, method 1. However, since there was considerable lack of concordance in duplicate determinations, and since this correction is not applicable to rosin, if present, it seems preferable as a general procedure to assume that the percentage of fatty acids obtained equals the percentage of oil in the sample, making no further correction. The average results with varnishes A to G, when thus calculated, as shown in Table 15, method 2, are correct to within 7 per cent of the predominating ingredient of the ash-free nonvolatile portion, and the greatest error for percentages of oil and of resin, when expressed as percentage of the varnish, is 2.2 per cent.

Some analyses were made by the method outlined on page 23, but varying the solvent; e. g., the proportions of ethyl ether and petroleum ether, used to treat the mixture of fatty acid esters and resin acids after esterification. It was hoped that a mixture would be found which would give accurate results without the use of a correction factor. The results, as given in Table 16, show that an appropriate mixture for a long oil varnish, D, gave erroneous results with the short oil varnish, C.

TABLE 14
Analysis of Melted Resins

Resin	Yield of material which would be weighed as fatty acids	Resin	Yield of material which would be weighed as fatty acids
	Per cent		Per cent
Resins of varnish C.....	10.6	Sierra Leone copal.....	7.1
Resins of varnish D.....	4.8	Kauri.....	4.7
Pontianak.....	3.1	Zanzibar.....	3.1
Manila.....	4.0	Dammar ^a	6.6

^a Not melted.

TABLE 15
Average Results from Table 13, Corrected

Varnish	Oil			Resin			
	Present	Found		Present	Found		
		Method 1	Method 2		Method 1	Method 2	Resin acids + unsapon. matter $\times 1.07$
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
A.....	3.9		4.5	48.6		48.0	
B.....	31.9		29.2	12.5		14.7	
C.....	16.1	17.2	18.0	29.7	28.6	27.8	28.8
D.....	36.1	35.9	34.9	16.3	16.5	17.5	16.9
E.....	26.2	25.9	25.3	23.2	23.5	24.1	22.1
F.....	36.1	36.4	35.4	15.0	14.7	15.7	14.2
G.....	27.6	27.8	27.6	21.5	21.3	21.5	20.1

TABLE 16
Effect of Varying Solvent Used after Esterification

Experiment	Varnish	Solvent	Oil		Resin				
			Present	Found, fatty acids $\times 1.06$	Present	Found			
						Insoluble resin	Soluble resin acids + unsapon. matter	Total resin	Total resin by difference
			Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1.....	D	Ether.....	36.1	37.4 37.9	16.3	0.0	15.3 14.5	15.3 14.5	15.0 14.5
Average				37.7			14.9	14.9	14.7
2.....	D	Ether 4/5, petroleum ether 1/5	36.1	34.7 35.4	16.3	0.0	17.6 16.1	17.6 16.1	17.7 17.0
Average				35.1			16.9	16.9	17.3
3.....	D	Ether 1/2, petroleum ether 1/2	36.1	34.7 34.5	16.3	3.9 3.4	13.2 14.2	17.1 17.6	17.7 17.9
Average				34.6		3.7	13.7	17.4	17.8
4.....	D	Petroleum ether	36.1	34.3 34.2	16.3	9.3 9.4	8.6 8.0	17.9 17.4	18.1 18.2
Average				34.3		9.4	8.3	17.7	18.1
5.....	C	Ether 4/5, petroleum ether 1/5	16.1	20.0	29.7	7.6	18.6	26.2	25.8

(d) DISCUSSION OF ESTERIFICATION METHODS.—The results obtained with the short oil varnish, C, using the methods of Darner and McIlhiney, indicate that with certain samples these methods will give accurate results for percentages of oil and resin. With the long oil varnish, D, in which the mix was bodied by heating for several hours, these methods gave very poor results. The chief error in using methods which involve the use of petroleum ether lies in the assumption that the precipitates obtained with all samples consist of all the "gum" present and no oil.

Assuming that the neutralization values of the portions of the hard resins that are dissolved by petroleum ether are low, the volumetric determination of rosin in the presence of other resins may give fairly accurate results. In many cases analysts may have obtained accurate results by various methods for the determination of oil, rosin, and "hard gum," because of compensating errors.

The changes which occur when varnish is aged must be considered in connection with the determination of oil and resin. The oil may oxidize and thereby gain in weight, causing a yield of fatty acids which will be greater than that from the freshly prepared varnish. Turpentine, if present, may change so as to yield nonvolatile matter which will appear on analysis as resin or oil, probably as the former. Unless the varnish is in closed containers the volatile thinner will, of course, evaporate, causing a higher yield of nonvolatile matter.

V. PROPOSED METHOD

The following method, already outlined on page 23, is proposed for the determination of oil and resin, since in the experimental work it was found to be the most reliable as a general method for different types of oil varnish. The essential steps in the process are outlined in the following diagram (Fig. 1). In the following description of the method, as used by the author, the exact details may not be essential, but are given as a guide for those not familiar with varnish analysis.

To 3 to 4 grams of varnish in a flask add about 25 cc of water and boil until the volume of the water is about 10 cc. This removes nearly all of the volatile thinner. Add 25 cc of 0.5 N

alcoholic potash and 25 cc of benzene (C_6H_6) and boil under a reflux condenser for one-half hour. Evaporate the solution to about 15 cc and add about 10 cc of alcohol. Transfer the mixture completely to a separatory funnel, washing the flask with water and ether, using a policeman if necessary. After diluting with water to about 100 cc add 100 cc of ether and shake. (At this point, and with all subsequent extractions with ether, add alcohol in 2 cc portions, if necessary, to cause the layers to separate.) Having drawn off the aqueous layer, wash the ether layer three times with water, and finally transfer the ether solution, containing part of the unsaponifiable matter, to a tared flask for future use if so desired (see diagram). To the combined soap solution and washings add an excess of hydrochloric acid and extract twice with 50 cc of ether. Discard the aqueous layer, wash the combined ether solution with water, transfer it to a flask, and distil off the ether. To the dry residue add 20 cc of absolute alcohol and 20 cc of a mixture of 1 volume of sulphuric acid and 4 volumes of absolute alcohol and boil the mixture for two minutes under a reflux condenser. Completely transfer the contents of the flask to a separatory funnel (a small amount of insoluble matter may be obtained here), washing the flask with water and ether. Add 100 cc of ether and after agitation add 100 cc of 10 per cent sodium-chloride solution and again agitate. Draw off the aqueous layer, extract it with 50 cc of ether, and wash with water the combined ether solutions. To the latter add 50 cc of 0.2 N potassium hydroxide solution and 10 cc of alcohol, shake the mixture, and draw off the lower layer into a second funnel. Wash the ether layer with 50 cc of water containing 5 cc of 0.2 N potassium hydroxide solution and 5 cc of alcohol. If, on treating the ether solution of the resin acids and fatty acids esters with the potassium hydroxide solution, some insoluble matter is formed, it is due to the insolubility of the soaps of the resin acids, and such matter is carried through into the final resin soap solution, where it is decomposed with acid. Extract the combined aqueous portions with two 50 cc portions of ether and finally wash the combined ether solutions (containing the ethyl esters of the fatty acids) with water. Distil off the ether and boil the residue with 25 cc of 0.5 N alcoholic potash for one-half hour under a reflux condenser. Transfer the

solution to a separatory funnel, washing the flask with ether and water, and extract the soap solution four times with ether. Wash the combined ether solution twice with water and add it to the first ether solution of unsaponifiable matter obtained. (The determination of unsaponifiable matter may be omitted unless a check

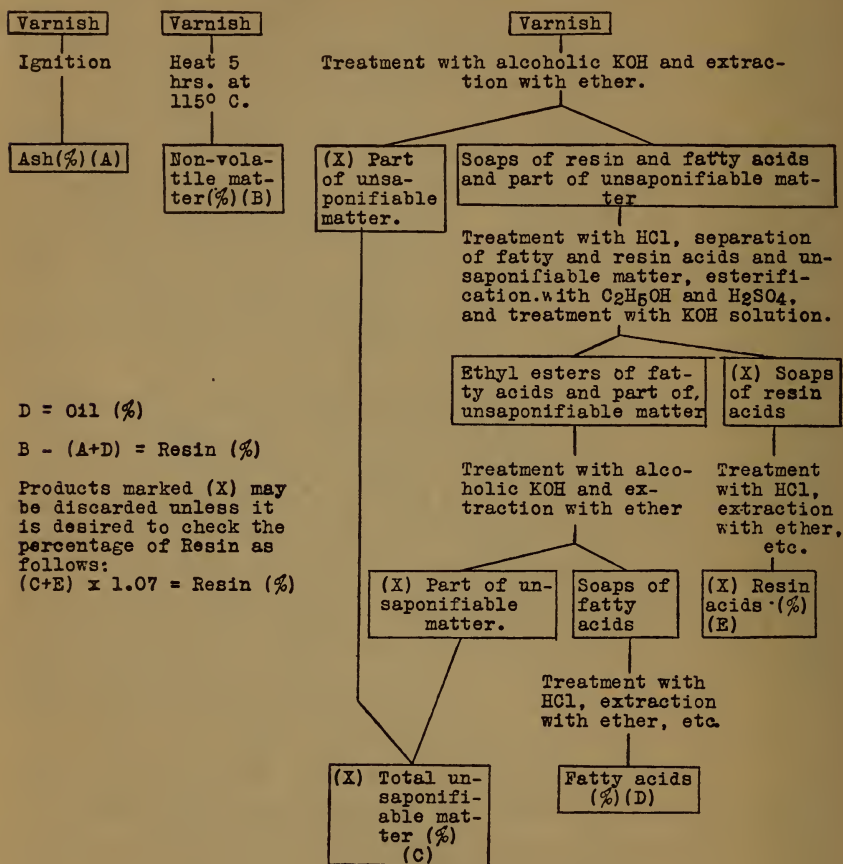


FIG. 1.—Diagram of proposed method

on the percentage of resin obtained by difference is desired.) Unite the solution and washings containing the soaps of the fatty acids. Add an excess of hydrochloric acid and extract twice with ether. After washing the combined ether solution with water, transfer it to a tared flask, distil off the ether, dry the residue to constant weight at 110° C, and weigh as "fatty acids." If the

determination of resin is desired, to the combined aqueous solution and washings (containing the resin soaps) add an excess of hydrochloric acid, extract twice with ether, wash the combined ether solutions twice with water, and then distil off the ether. Dry the residue to constant weight at 110° C and weigh as "resin acids." The Twitchell method of esterification may be substituted for the Wolff method.

Calculation: Report the percentage of fatty acids obtained as percentage of oil and calculate the percentage of resin by difference. Multiply the sum of the unsaponifiable matter and resin acids by 1.07 to obtain a check result for the percentage of resin. (The error introduced by omitting to correct for the percentage of unsaponifiable matter in the oil is so small that it may be ignored.) Alternative method of calculation in the absence of rosin: Multiply the percentage of fatty acids obtained by 1.06 and subtract the product from the percentage of ash-free nonvolatile matter. Multiply the result by 1.07 to obtain the percentage of resin. Calculate the percentage of oil by difference.

VI. SUMMARY

(1) The glycerol yields of varnishes, determined after saponification with aqueous potassium hydroxide solution, when multiplied by 10, gave figures which were fairly close to the amounts of oil present, except with a varnish containing Chinese wood oil, in which case the results were low.

(2) When varnishes, or the portions of varnishes soluble in petroleum ether, or the mixtures of unsaponifiable matter, fatty acids, and resin acids (separated from varnishes), were oxidized by heating thin films for eight days at 100–110° C, subsequent extraction with chloroform removed only a portion of the resinous matter present, except with a sample the nonvolatile portion of which was mainly rosin. Thus, erroneous results were obtained by the methods of Voorhees and of Livache and McIntosh.

(3) When varnishes were treated with an excess of petroleum ether, as in Voorhees's method, the precipitates obtained consisted principally of resinous matter, but contained some oil. The presence of Chinese wood oil raised the oil content of the precipitate.

(4) When varnishes were saponified, treated with acid, and the resulting mixture of unsaponifiable matter, fatty acids, and resin acids were treated with an excess of petroleum ether, as in McIlhiney's method, the precipitates obtained contained a portion of the resin present in the varnish and a small amount of fatty acids.

(5) When varnishes were extracted with petroleum ether and the petroleum ether solution was subsequently cooled, as in Darner's method, the yields of total insoluble matter were less than the amounts of resin present in the samples.

(6) As methods for the determination of total oil and resin, McIlhiney's method (when treatment of the precipitate with 85 per cent alcohol was omitted) and Darner's method gave results with a short oil varnish which were fairly accurate, but both methods with long oil varnish gave high results for total resin content and low results for oil content.

(7) The proposed method for the determination of oil and resin, involving esterification by the Twitchell or Wolff methods, the use of ether as solvent after esterification and correction of the figures by appropriate factors, gave results which were sufficiently accurate for practical purposes, and appears to be the best method so far devised for general use.

WASHINGTON, September 14, 1915.



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